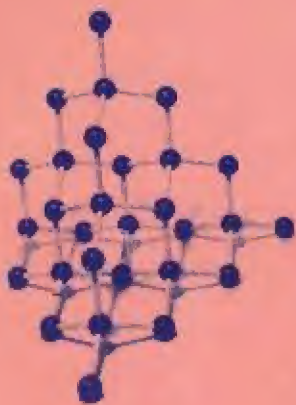


Chemistry Background Book



The Structure of Substances



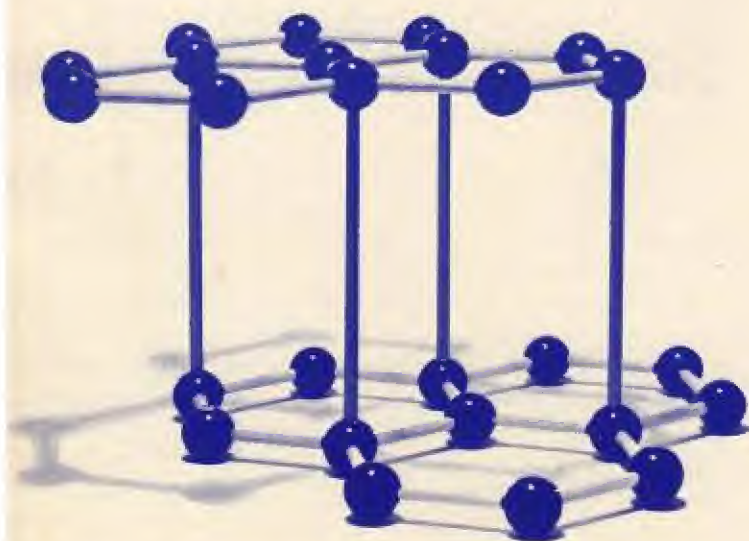


Model showing the way in which the carbon atoms are arranged in diamond.

Diamond – a hard glass-like substance.



THE IMPORTANCE of STRUCTURE



Model showing the way in which the carbon atoms are arranged in graphite.

Graphite — a soft, black substance.

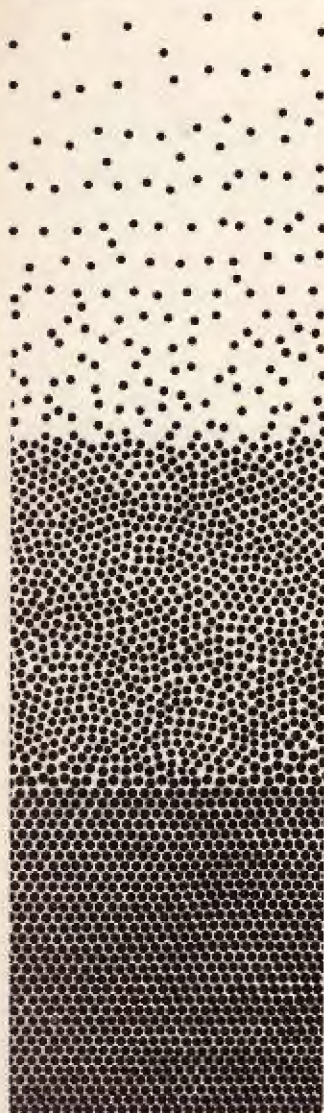


Look at the structures on these two pages. One is of diamond and the other of graphite. Both substances are composed of carbon atoms but, as you can see, the atoms in the two substances are arranged in very different ways. In diamond the atoms link together to form an interconnecting three-dimensional network. In graphite, the atoms form sheets of six-membered rings. Diamond is hard and glassy; graphite is soft and black. Since the atoms in both are the same, these differences between the properties of the two substances must stem from the different arrangement of the atoms. It is because structure helps to account for the properties of substances that it has become so important to the study of chemistry.

A hundred years ago, people could only make guesses as to how the atoms were arranged in substances. The regular shapes of crystals often provided them with useful clues, but they had no systematic way of finding out.

Then, in 1912, the German scientist von Laue reported that a beam of X-rays, on passing through a crystal, would form a pattern of spots on a photographic plate. In the same year W. L. (now Sir Lawrence) Bragg and his father Sir William Bragg showed how these patterns of spots (diffraction patterns as they are now called) could be used to determine the positions of the atoms in a crystal (see the Background Book, *The Start of X-ray Analysis*). The chief thing to understand about X-ray analysis is that it is possible to draw conclusions from a pattern of spots, which can be seen, about an arrangement of atoms, which cannot be seen. Using X-rays, the structures of thousands of substances have been investigated. In this book we look at a few of the more common structures of substances to be found in nature and in man-made products.

Solids Liquids AND GASES



In a gas, the atoms (or molecules) are widely separated and free to move.

In a liquid, the atoms (or molecules) are tightly packed but free to move.

In a solid, the atoms (or molecules) are tightly packed together and held in fixed positions.

The most obvious features of the way that the atoms are arranged in a substance depend on whether it is in the solid, liquid, or gaseous state.

The atoms in a solid must be held in fixed positions, for otherwise solids would not retain their shapes; they would crumble into a heap of molecules or atoms, which is what happens when a solid melts. Moreover, the atoms in a solid must be packed very tightly together. This is evident from the fact that solids are very difficult to compress. Even at pressures of thousands of tons per square inch, the change in volume is very small indeed. Increase in pressure cannot bring the atoms any closer together except by compressing or distorting the atoms themselves.

In most liquids (water is one of the exceptions), the atoms are less tightly packed than in a solid. This is evident if the substance is melted – there is usually an increase in volume on the change from solid to liquid, as you can check by looking up some substances in your *Book of Data*. Nevertheless, since liquids are also difficult to compress, the atoms must still be very close together. The main difference between solids and liquids is that liquids have no shape. They take the shape of their container and are free to move about and can be poured. Obviously the atoms in a liquid are not fixed in any definite position. They are able to move about, rolling over each other like grains of fine sand.

Gases not only take the shape of the vessel which contains them but also spread out to occupy the whole vessel; this is easily seen by using a coloured gas such as chlorine or bromine. Our picture of a gas is one in which the particles are free to move about and there are quite large spaces between them. If this is correct, then increasing the pressure should bring the particles as close together as they are in a liquid. The gas will then change to a liquid. Many substances that are gaseous at room temperature (such as ammonia and sulphur dioxide) can be liquefied by increasing the pressure, but others (such as oxygen and nitrogen) must be cooled as well as compressed. Cooling is necessary in order to slow down the rapid movement of the gas particles which tends to oppose the changing of the gas into liquid.

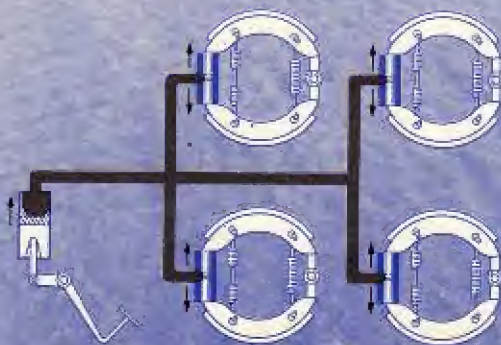
In this book we are concerned with the way in which atoms are arranged in solids and we look at them as crystals, as metals, as non-metallic elements, as ionic and other compounds, and as giant molecules.



Gases fill the container that holds them and, up to a certain point, are relatively easy to compress. This balloon is filled with hydrogen which is lighter than air and keeps it afloat.



Solids keep their shape and are very difficult to compress. The Firth of Forth bridges stay up because of this property of solids. *Radio Times Hulton Picture Library.*



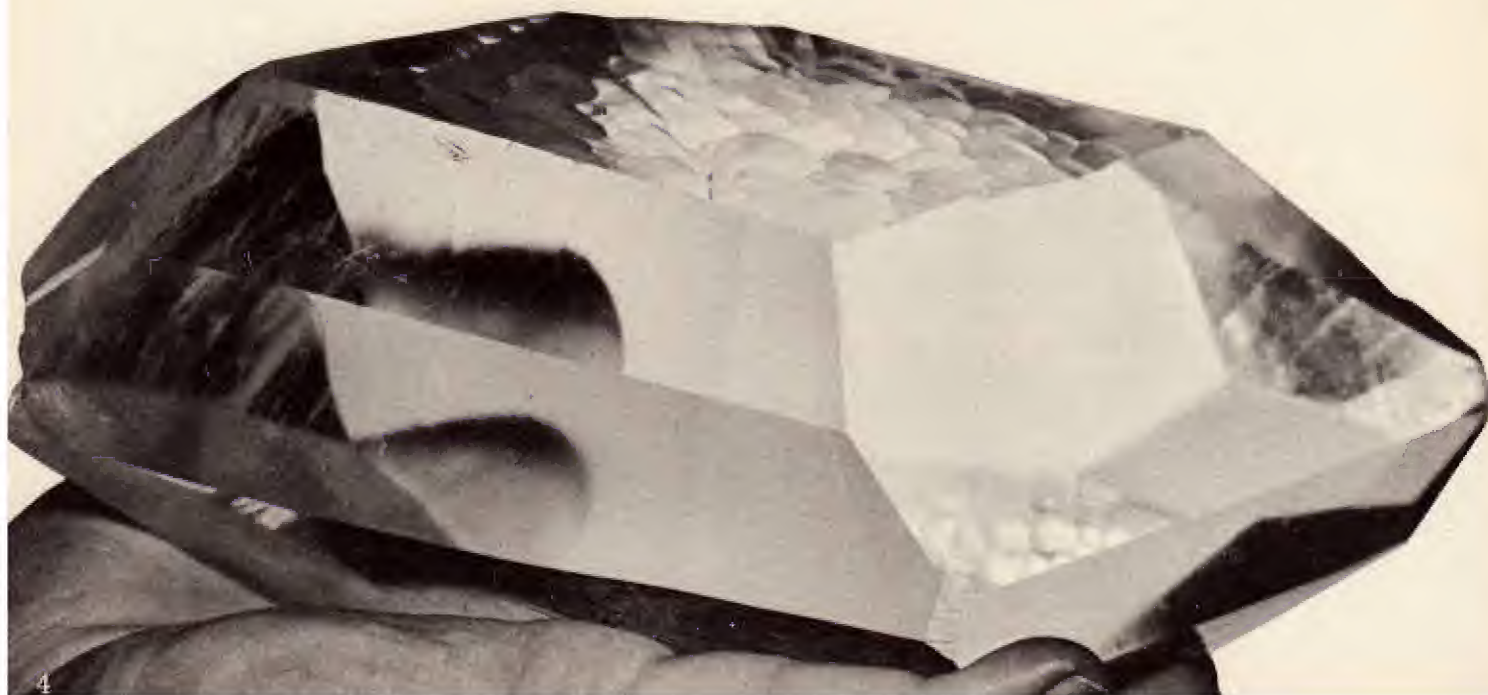
Liquids take the shape of the container that holds them. Like solids they are difficult to compress. In hydraulic brakes force is transmitted from the foot pedal to the brake drums by the liquid. Liquids are as strong as metal rods might be and can carry forces round bends and corners in ways that solids cannot. *Lockheed Hydraulic Brake Company Ltd.*

CRYSTALS: THE PACKING OF PARTICLES

Long before the discovery of X-rays, it was realized that the atoms in crystals were probably arranged in an orderly pattern. How else could the regularity of crystal shapes be explained? If crystals are observed growing under a microscope, this orderliness is even more striking. And if a crystal is broken it cleaves cleanly into lumps which resemble in shape the original crystal. Rock salt cleaves to form cubic-shaped crystals. Quartz cleaves to form hexagonal-shaped crystals.

Depending on the substance, crystals are built up of atoms,

This synthetic quartz crystal was grown in a laboratory pressure vessel in a few weeks. It might have taken as many years for it to grow naturally.
Roditi International Corporation Ltd.



ions, or molecules. We can get some idea of the different ways in which these particles may be packed in a crystal by building up structures with polystyrene spheres or ping-pong balls. The accompanying illustrations show four basic structures which, as we shall see in the next few pages, represent the packing of the particles in a number of well-known substances.

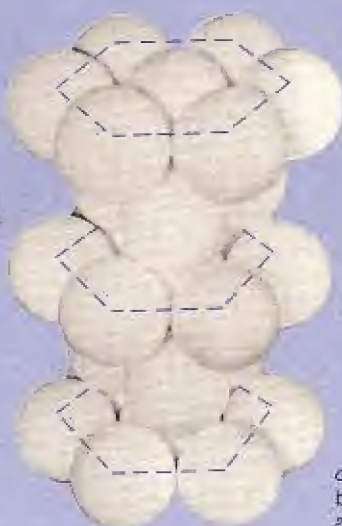
In the first two – face-centred cubic packing and hexagonal close packing – each particle is surrounded by twelve others. This is described as 12-coordination, and

represents the closest possible packing of the particles. In the third structure, body-centred cubic packing, each particle is surrounded by eight others (8-coordination), and in the fourth, the tetrahedral structure, each particle is surrounded by four others (4-coordination). The packing of the particles in these last two structures is much more open, and therefore a given number of particles occupies a greater volume than in the other two structures. It follows that the packing of the particles in a substance affects its density: the closer the packing, the greater the density.

Packing of particles in crystals:



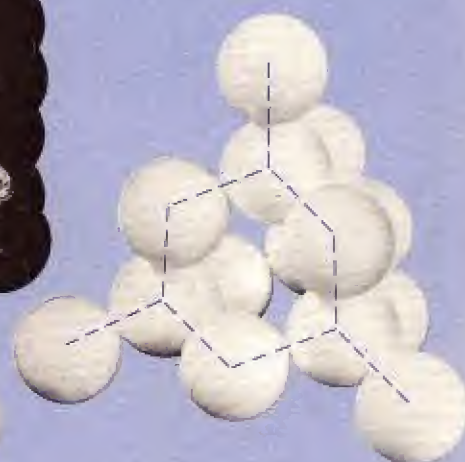
a. Face-centred cubic packing – built up of cubes with a sphere at the centre of each face. Each sphere inside the structure is surrounded by twelve other spheres in contact with it.



b. Hexagonal close packing – built up of layers of hexagons. Again each sphere inside the structure is surrounded by twelve other spheres in contact with it.



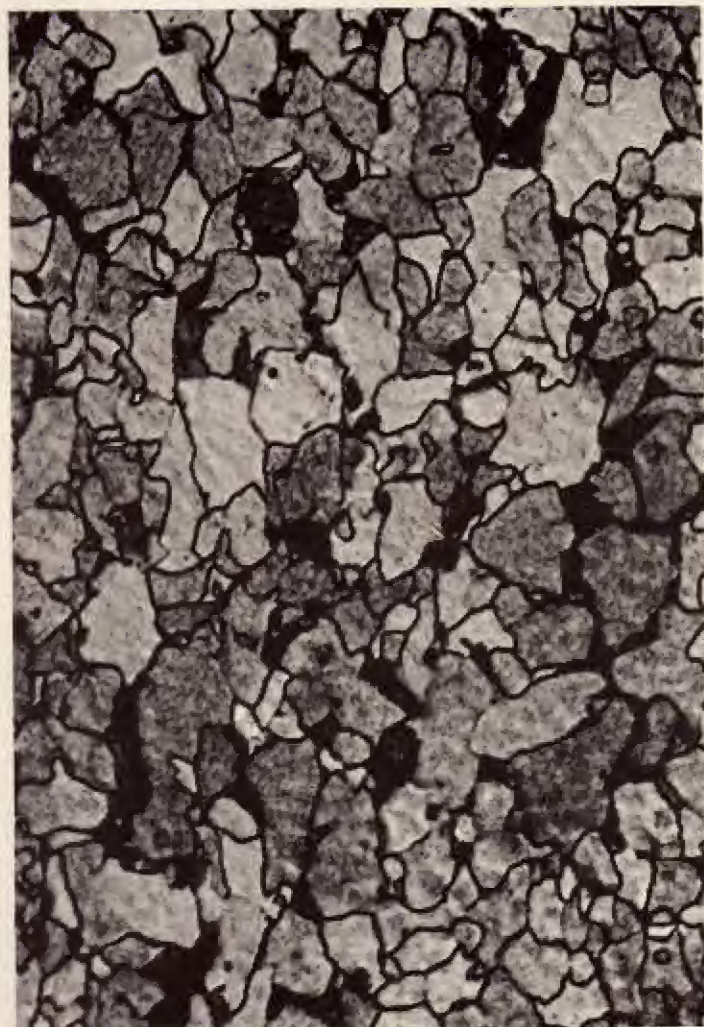
c. Body-centred cubic packing – built up of cubes with a sphere at the centre and a sphere at each corner. Each sphere inside the structure is surrounded by only eight other spheres in contact with it, and consequently this is a more open type of packing.



d. Tetrahedral packing – built up in such a way that each sphere forms the centre of a regular tetrahedron, whilst the four spheres surrounding it have their centres at the four corners of the tetrahedron. This again is a more open kind of packing.

METALS

Crystal grains in steel, an alloy of iron and carbon. In metals, the crystals are irregularly shaped, but the packing of the atoms in the crystals always follows a regular pattern. *BISRA*



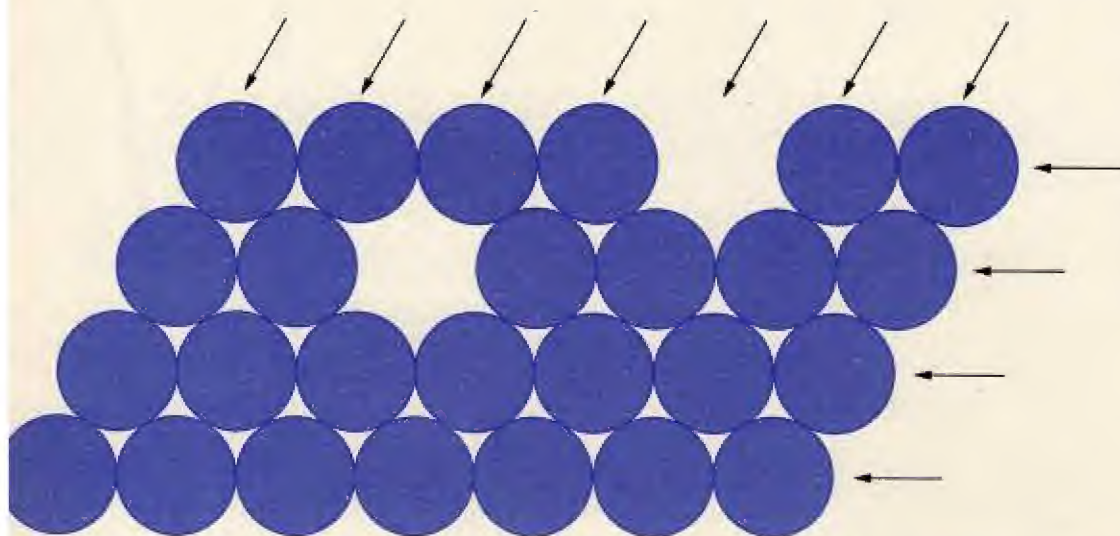
Over three-quarters of the chemical elements are metallic. At first, it is not obvious that metals are composed of crystals: they are not granular materials like salt or sugar. However, if a metal is examined under a microscope, it is seen to be made of small irregularly shaped crystalline grains. X-ray analysis shows that the packing of the metal atoms in these grains may be any of the forms described on the previous page. It depends on the metal. Copper has a face-centred cubic structure; chromium has a body-centred cubic structure; zinc and magnesium have a hexagonal structure; a few metals such as tin and germanium have a tetrahedral structure.

Some metals may have one of these structures at room temperature and change to another at a higher temperature. Iron, for example, normally has a body-centred structure but, at temperatures above 910°C , changes to a face-centred structure and then, above 1400°C , reverts back to the body-centred structure. Why a metal has one structure rather than another is not properly understood.

Two of the most useful properties of metals are that they are *ductile* (they can be pulled out into wires) and *malleable* (they can be rolled into sheets or hammered into shape). The way in which the particles of most metals are built up into layers helps to explain these two properties. When a force is applied to a metal it causes the layers to 'slide' over each other. The particles break the bonds that hold them together, slip into a new position, and re-establish their bonds.

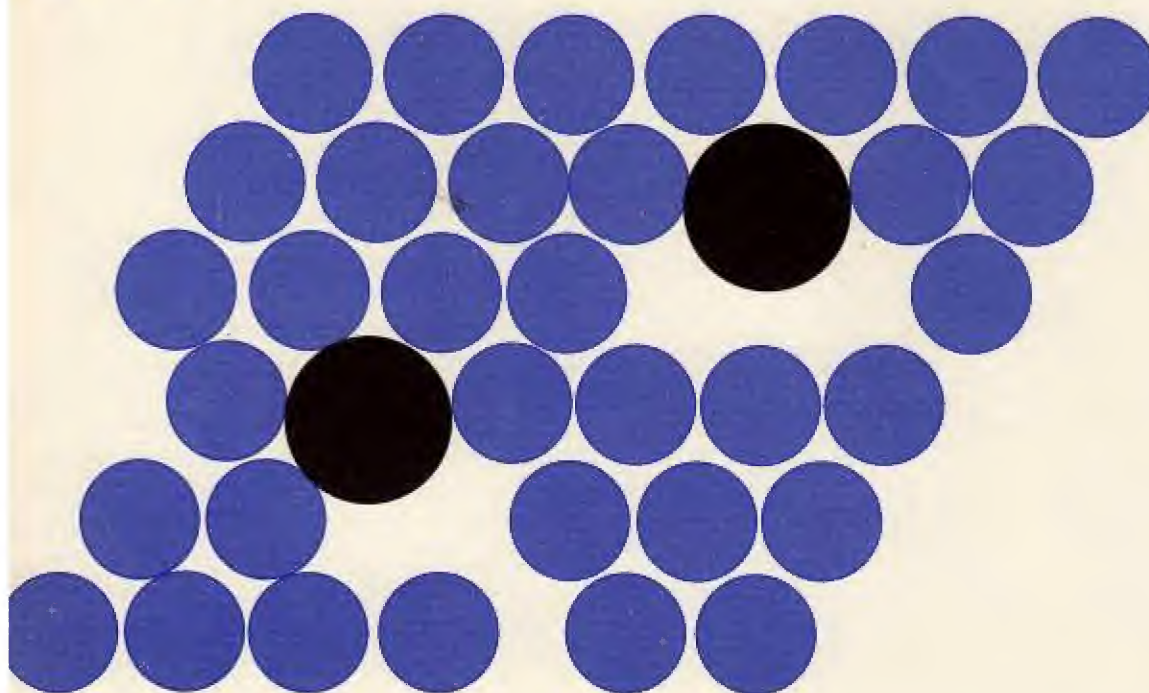
One of the ways of strengthening a metal and so preventing the layers from slipping is to 'alloy' it with small quantities of another element, for example, putting zinc in copper to make brass. Particles of the alloying element are of a different size (atomic volume) from the main metal, and therefore obtrude in the orderly layers of particles, hindering them from sliding over each other.

Naturally it is not necessary to understand the structure of metals to make alloys: bronze, an alloy of copper and tin which is much stronger than either of the two alloying metals, has been known for thousands of years. Nevertheless, without this knowledge it would be very difficult to produce the many hundreds of special alloys that are used in industry today.



possible glide planes

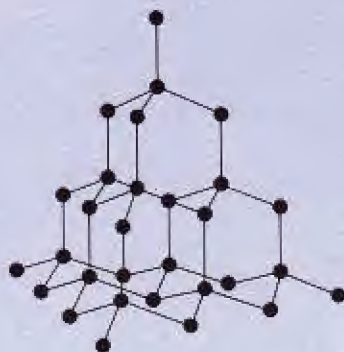
Force applied to a metal crystal causes the layers of atoms to slide over each other. This is known as 'slip'.



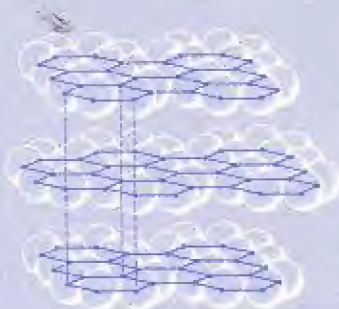
Atom of an alloying element in a metal structure. The presence of this 'foreign' atom hinders the metal layers from sliding over each other and thereby toughens the metal.

Non-Metallic Elements

In diamond, the atoms are packed tetrahedrally – a structure that would result from puckering the flat rings in graphite. There are no layers of atoms as there are in graphite and in most metals, and therefore the atoms cannot slide over each other. This is one of the main reasons why diamond is so hard.



In graphite, the atoms form flat layers of six-membered rings. The forces between the layers are weak, and therefore the layers can slide very easily over each other. This is why graphite is soft and flaky.



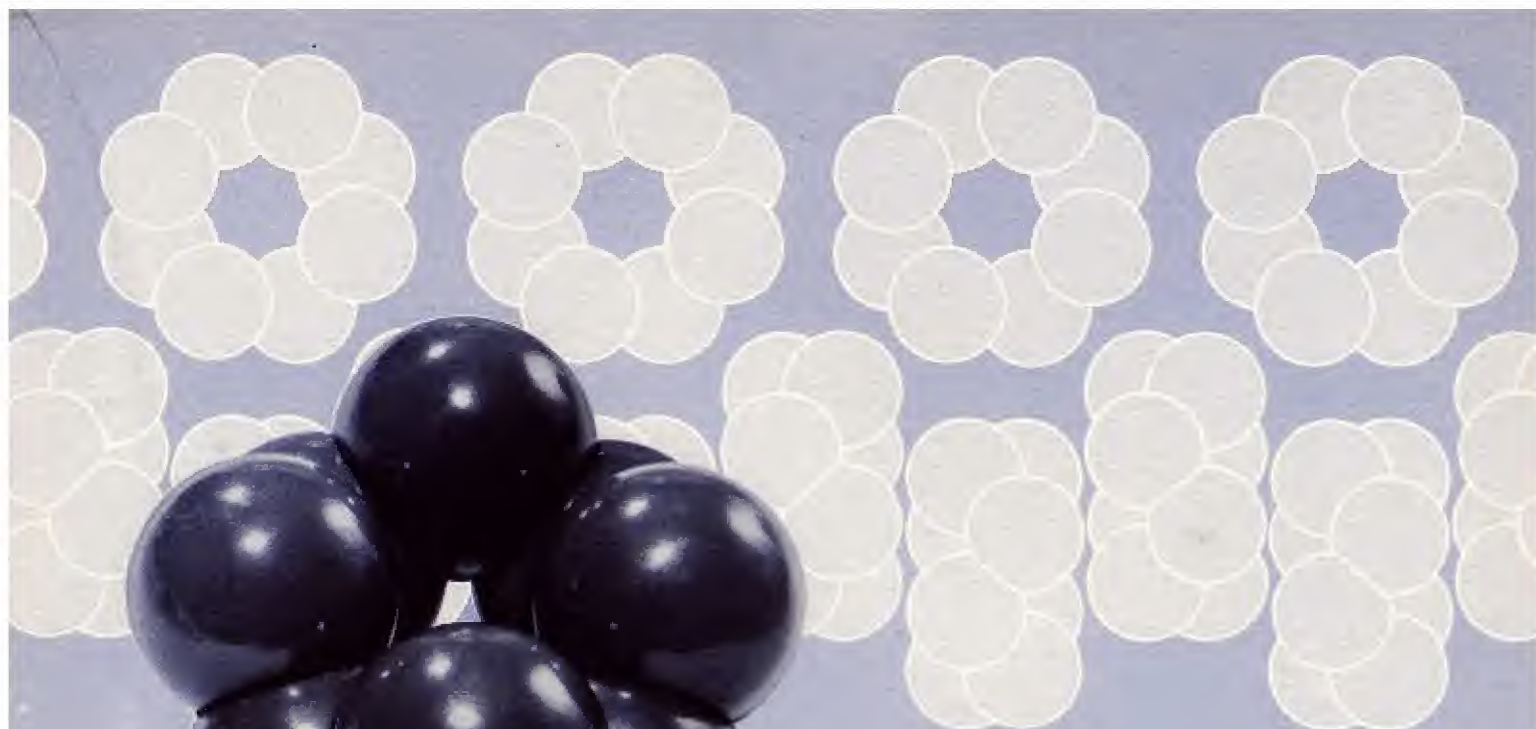
Many of the non-metallic elements are gases at room temperature. To convert them into solids, they have to be cooled often at very high pressures and down to very low temperatures. With the exception of helium, the inert gases crystallize in a cubic close-packed structure. Hydrogen, which freezes at about minus 260°C , has a hexagonal close-packed structure; the particles are not single atoms, as with the inert gases, but molecules, each containing two hydrogen atoms.

As we saw at the beginning of the book, the non-metal carbon has two crystalline forms, diamond and graphite. It also has a non-crystalline or 'amorphous' form, charcoal, in which there are areas of disorder in the arrangement of the atoms.

In the diamond crystal the atoms are packed tetrahedrally. Each carbon atom may be thought of as being at the centre of a tetrahedron, surrounded by four other carbon atoms with their centres at the corners of the tetrahedron (see the model on page 5). The particles are not in layers and therefore, unlike the particles in most metals, cannot slide over each other. This partially accounts for the hardness of diamond.

The structure of graphite is unique among the elements. Carbon atoms form layers of six-membered rings. These are separated from each other by a distance which is about two-and-a-half times as great as the distances between the centres of the carbon atoms in the layers. The forces between the layers are very weak, and hence the layers can slide very easily over each other. This accounts for the use of graphite in pencils and as a lubricant. Also, the space between the layers is large enough to hold other atoms or groups of atoms and explains why graphite is sometimes used as an absorbent.

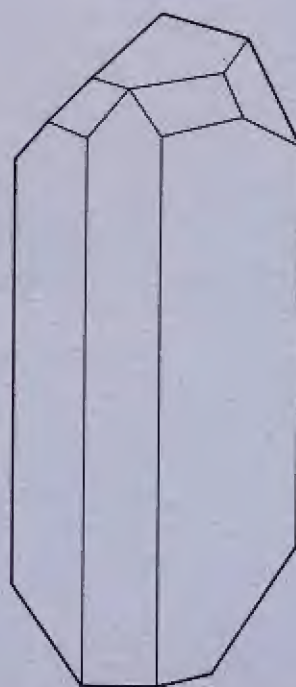
Another element that exists in more than one solid form – *allotropic* forms, as they are called – is sulphur. At room temperature the most stable crystal form is rhombic or alpha sulphur (see the opposite page). The crystals result from the packing together of ring-shaped sulphur molecules, each consisting of eight atoms linked together. When rhombic sulphur (melting point 115°C) is heated, it forms a honey-coloured liquid composed of the ring-shaped molecules. On cooling, the liquid sulphur forms needlelike crystals known as monoclinic or beta sulphur. This is the stable form of solid sulphur at temperatures above 96°C , and the way the molecules are packed together clearly differs from the rhombic.



The sulphur molecule – a ring of eight sulphur atoms linked together.



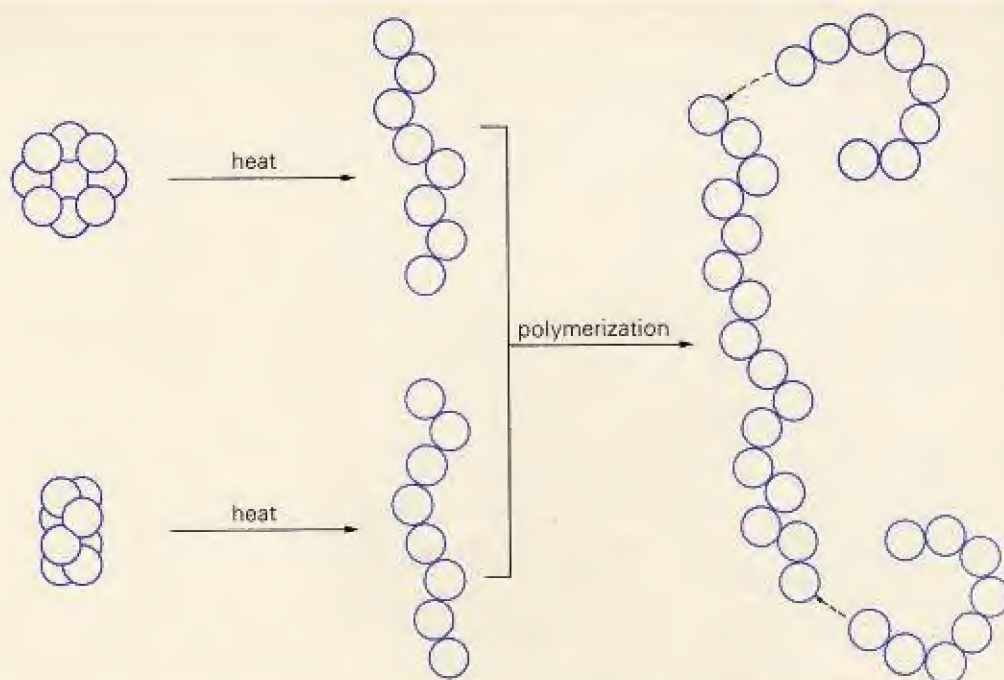
A crystal of rhombic sulphur – the stable form of solid sulphur at temperatures below 96°C.



The packing of sulphur molecules in a sulphur crystal – the bulges of one molecule fit into the hollows of its neighbours.

A crystal of monoclinic sulphur – the stable form of solid sulphur at temperatures above 96°C.

The effect of strongly heating sulphur – the molecular rings open out to form chains and the chains link together or polymerize to form much larger chains. If the sulphur is then rapidly cooled, it solidifies as long chains to form plastic sulphur.



If, instead of being cooled, the temperature of the liquid is raised, the molecular rings open out to form chains which link together to form very much larger chains – it has been estimated that they may consist of as many as a million sulphur atoms. The liquid becomes red and sticky and, if rapidly cooled in water, the sulphur atoms do not have time to revert back to rings but solidify as long chains of atoms tangled together. This is known as plastic sulphur: it can be stretched, and its structure resembles the long-chain molecules of plastics referred to at the end of this book. Both monoclinic and plastic sulphur slowly change at room temperature to the rhombic form.

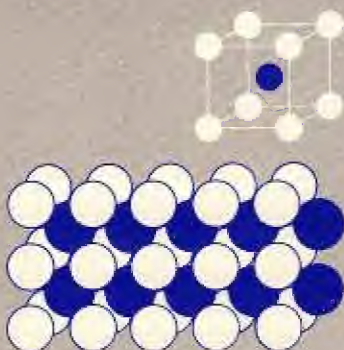


Plastic sulphur which can be stretched like rubber.

Ionic Crystals



The structure of caesium chloride – body-centred cubic packing with each caesium ion surrounded by eight chloride ions and each chloride ion surrounded by eight caesium ions.

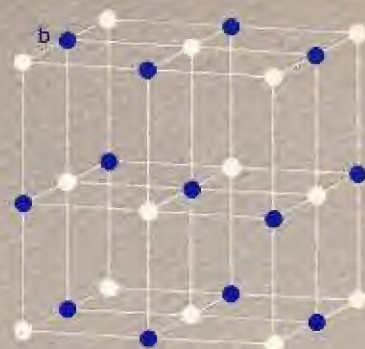


Many of the solid substances we meet in the laboratory are compounds formed by the combination of a metal with a non-metal, for example, the metal oxides, carbonates, sulphides, and chlorides. All of these are crystalline. They have high melting points, suggesting that there are strong bonds between the particles in the crystal. When molten, they are good conductors of electricity, suggesting that they are composed of charged particles called ions. The metal ions (cations) carry a positive charge and the non-metal ions (anions) carry a negative charge. It is believed that the attraction between the oppositely charged ions binds the particles together strongly in the crystal. In other ionic compounds, the ammonium ion (NH_4^+) takes the place of the metal.

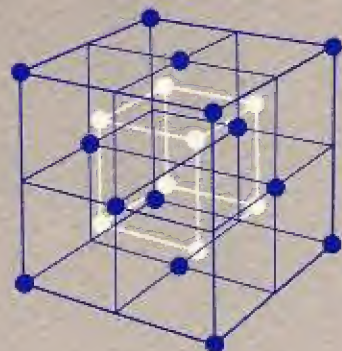
The first structures to be determined by X-ray analysis were the ionic crystals of potassium chloride and sodium chloride, although before the analysis it was thought that they were composed not of ions but molecules. Both substances were found to have face-centred cubic structures, with each metal ion surrounded by six chloride ions and each chloride ion surrounded by six metal ions. Cubic packing is what would be expected; the crystal shapes of both are cubes.

a. The structure of sodium chloride – two interpenetrating face-centred cubic structures, one of sodium ions and the other of chloride ions.

b. Each chloride ion is surrounded by six sodium ions and each sodium ion by six chloride ions. In this model the chloride ions are white and the sodium ions blue.



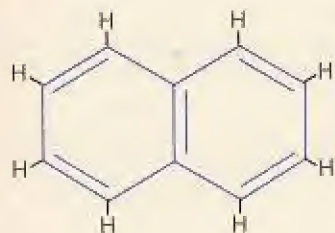
The structure of calcium fluoride (CaF_2) – the calcium ions form a face-centred cubic structure, and the fluoride ions are disposed tetrahedrally with respect to the calcium ions. Each calcium ion is surrounded by eight fluoride ions (at the corners of a cube) while each fluoride ion is tetrahedrally surrounded by four calcium ions.



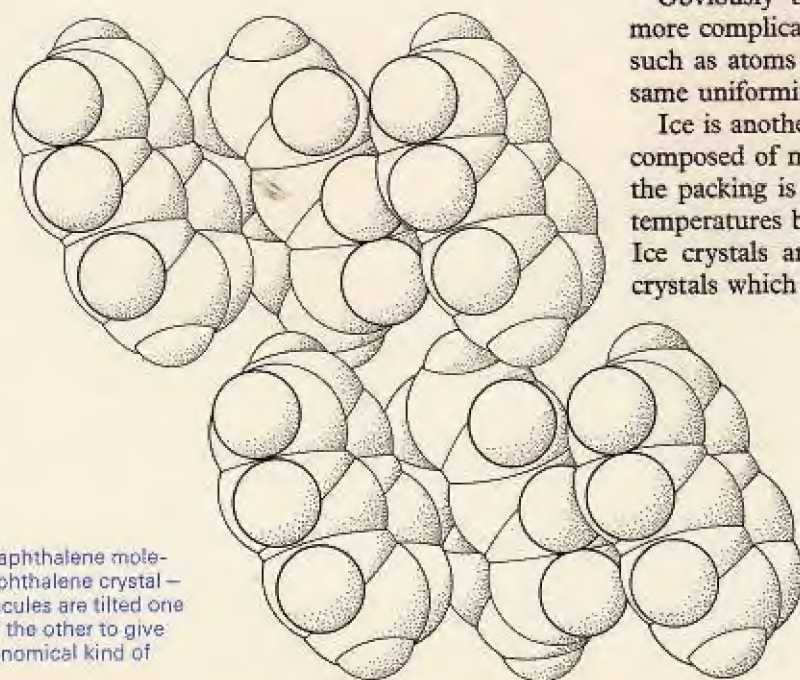
Among the thousands of ionic compounds there is a great variety of crystal shapes, and these shapes tend to reflect the packing of the ions in the crystals. In effect, each crystal represents a giant structure built up from a repeating pattern of the ions that it contains, rather like the decorations on wall-paper but in three dimensions.

An important distinction between ionic crystals and metallic crystals is that metals, being elements, are built up from particles of the same size, whereas ionic substances, being compounds, are built from particles of differing size. For example, the volume of the chloride ion is over ten times that of the sodium ion and therefore, to build an accurate model of the sodium chloride structure, we would have to use small beads to represent the sodium ions and ping-pong balls to represent the chloride ions (as in the diagram). Sometimes the ion may consist of several atoms (for example, the sulphate ion SO_4^{2-}), and here the difference in volume may be even more marked. This permits much greater variety in the packing of ionic crystals, such as the squeezing of small ions into the spaces between large ions and the incorporation of water molecules, called 'water of crystallization', in the ionic lattice.

OTHER CRYSTALLINE SUBSTANCES



A naphthalene molecule – consisting of ten carbon atoms and eight hydrogen atoms. The carbon atoms are arranged in a flat double ring with a hydrogen atom attached to each carbon atom except where the rings join.



Packing of naphthalene molecules in a naphthalene crystal – half the molecules are tilted one way and half the other to give the most economical kind of packing.

The structures of most of the solid substances that we have described so far are built up from atoms or ions. But many crystalline solids are composed of molecules, and in this sense they resemble more closely the majority of liquids or gases. Solid hydrogen and rhombic sulphur, both of them elements, are solids of this kind. Other elements in which the crystals are composed of molecules are phosphorus (P_4) and iodine (I_2).

Crystalline compounds whose structures are built from molecules are commonly found among carbon compounds. Unlike ionic crystals, molecular crystals are soft, have low melting points and, when molten, do not conduct electricity. Whereas ions are bonded together by strong electrical forces, the attraction between molecules is relatively weak. Naphthalene ($C_{10}H_8$) is a familiar organic solid with a crystalline structure. The molecules of naphthalene consist of two hexagonal rings of carbon atoms with hydrogen atoms attached, as shown in the diagram. The molecules are flat and in the crystal are closely packed although, as in iodine and sulphur, they are not parallel to each other: half are tilted one way and half the other.

Obviously the packing of these molecules presents far more complications than the packing of individual particles such as atoms or single ions. Nevertheless we still find the same uniformity in the packing as in other kinds of crystal.

Ice is another familiar substance in which the crystals are composed of molecules. They are packed tetrahedrally, and the packing is very open with the result that cold water at temperatures below 4°C is denser than ice.

Ice crystals are hexagonal. This is reflected in snowflake crystals which all exhibit hexagonal symmetry.

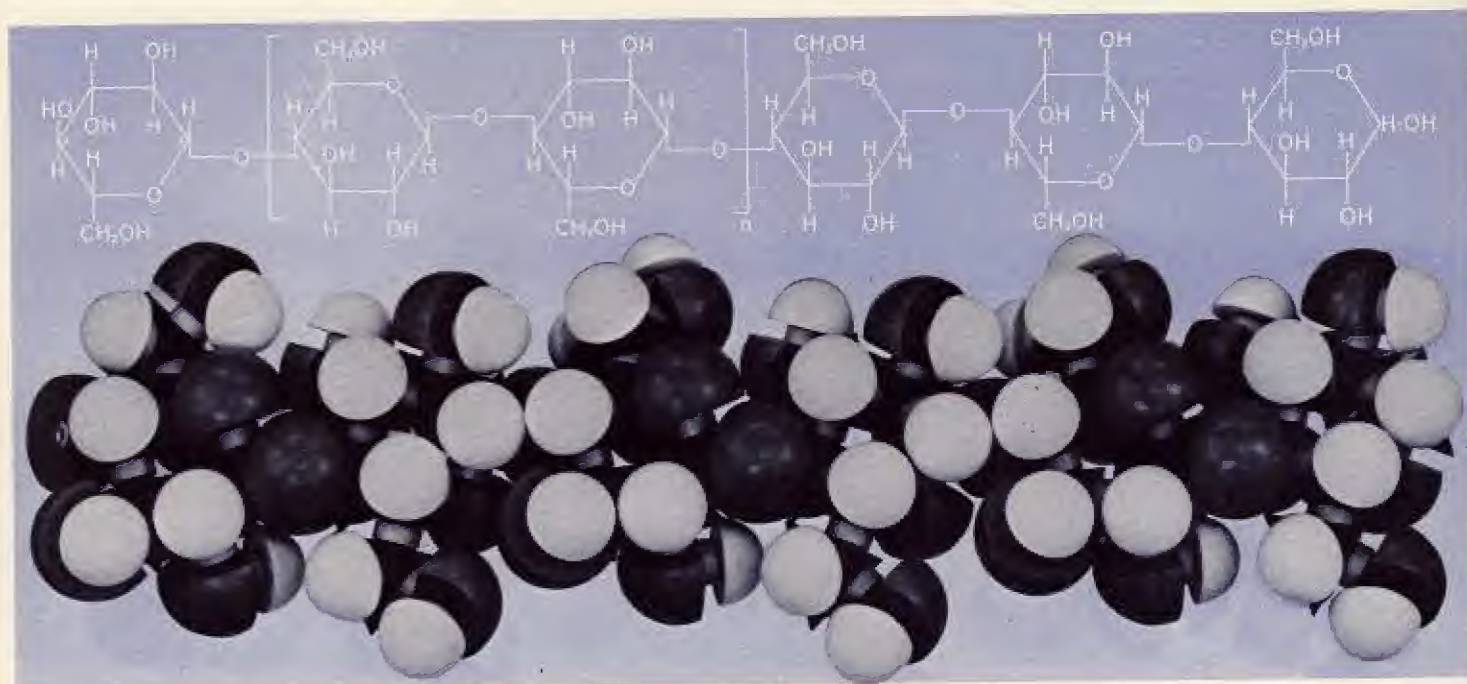
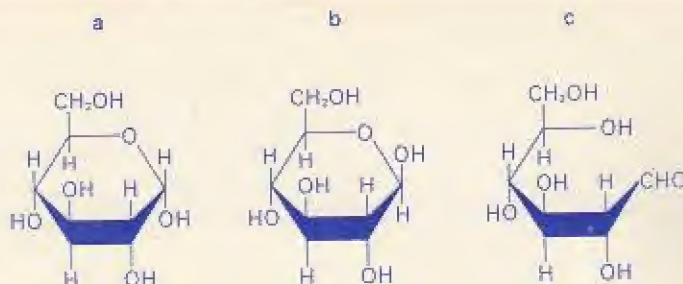
Snowflake crystals – a variety of shapes but all with hexagonal symmetry.



GIANT MOLECULES

- a Alpha-glucose molecule.
- b Beta-glucose molecule – see if you can tell the difference.
- c The aldehyde form of glucose – the shift of a hydrogen atom has caused the ring to open.

Chain molecule of cellulose – formed by the linking together of glucose molecules. *Courtaulds, Ltd.*

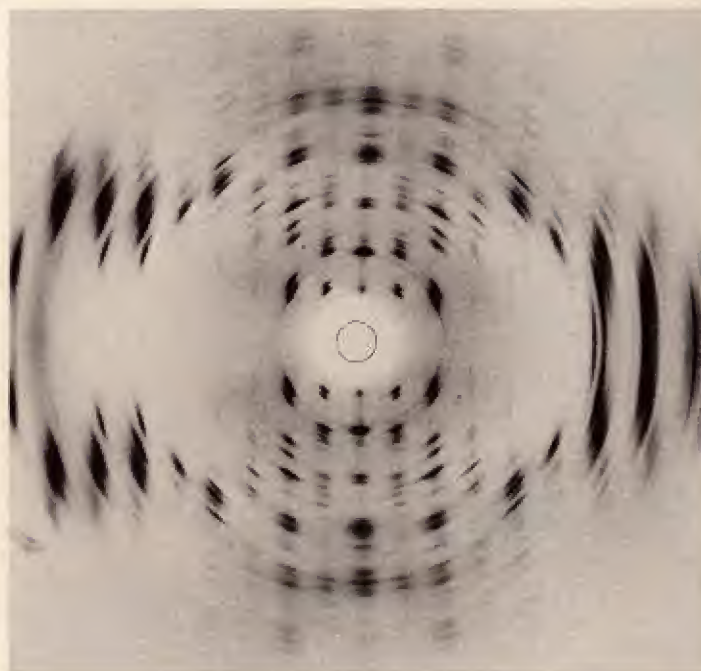
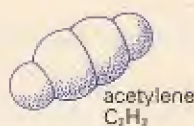
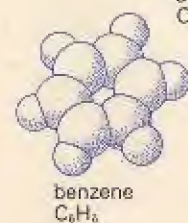
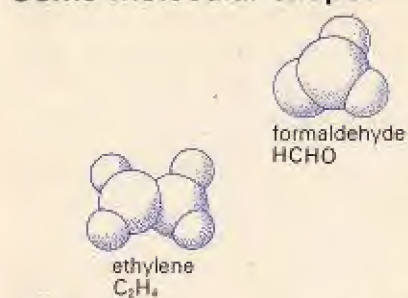


With very large molecules composed of hundreds or even thousands of atoms, as in plastics and such natural substances as cellulose, two problems suggest themselves: what are the different atoms in the molecule and how do they fit together? And how are the atoms arranged three-dimensionally in space? The way in which the molecules are packed together – structure as we have been considering it so far – may or may not be of importance; it depends on the substance.

The different atoms of which the giant molecules are composed are determined by chemical analysis or X-ray

analysis or, more often, both. Very many giant molecules are composed of chains of smaller molecules linked together in a repetitive pattern. To find out the composition of the giant molecules, it is only necessary to determine the composition of the smaller molecular units and, where there is more than one kind, the order in which they are linked together. Cellulose, for example, consists of chains of glucose molecules linked together, as shown in the diagram on this page. It is interesting to note that glucose has three molecular structures (see diagram), although the aldehyde form is

Some molecular shapes

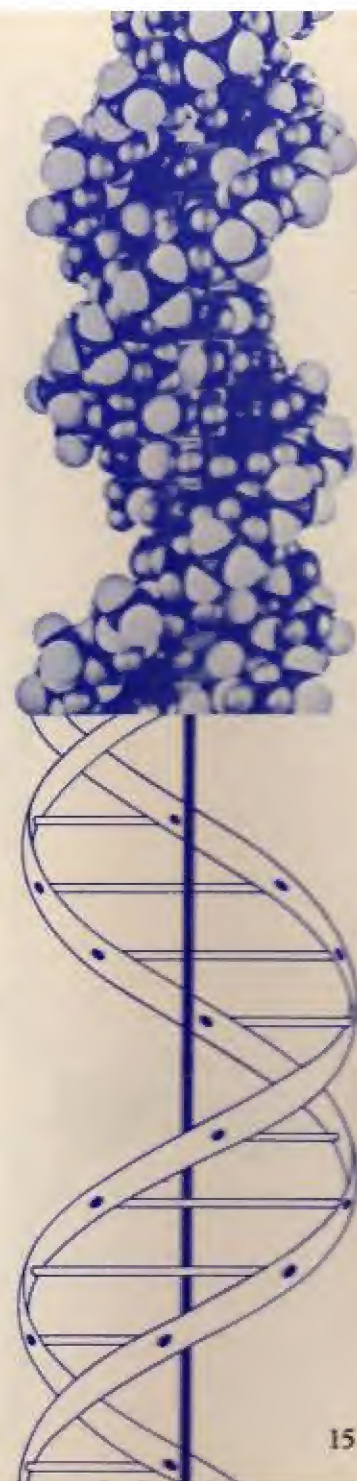


rarely found in the solid state. Alpha and beta glucose differ in the extent to which they rotate a beam of polarized light.

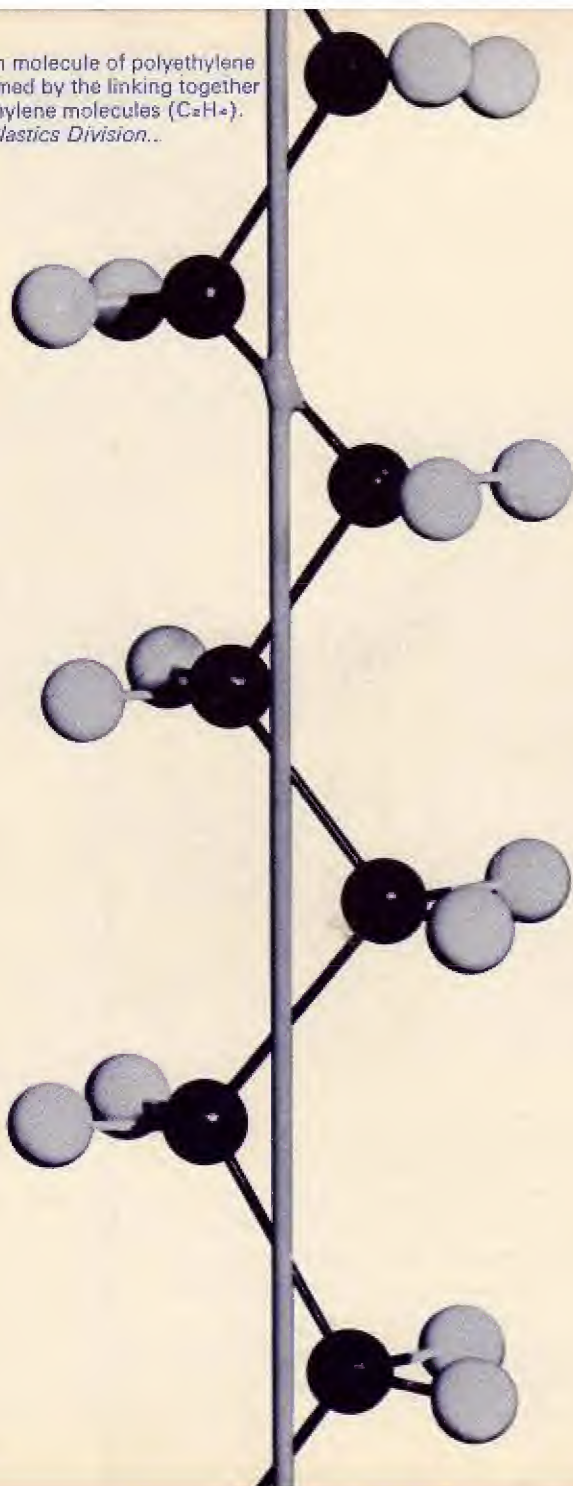
Working out the geometrical arrangement of the atoms in giant molecules demands detailed X-ray analysis combined with much hard thinking. The helical arrangement of DNA (deoxyribonucleic acid), the substance in the nucleus of living cells, was determined in 1954 by Francis Crick and James Watson, aided by the X-ray photography of Maurice Wilkins.

X-ray diffraction photograph of DNA which is in agreement with the idea of its structure as a double helix. *Dept of Biophysics, King's College London.*

The structure of DNA (deoxyribonucleic acid) – that of a double helix.



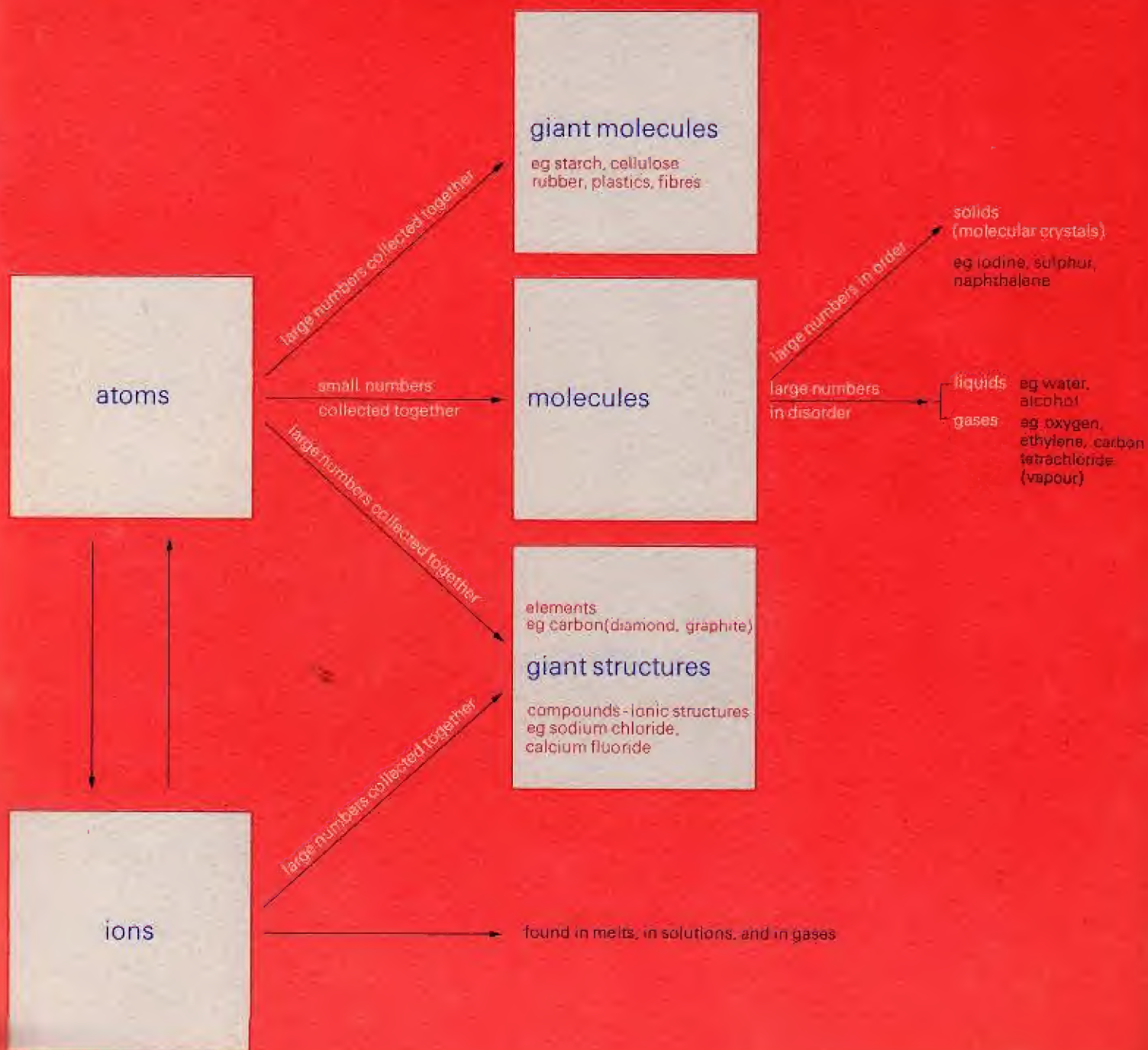
Chain molecule of polyethylene
— formed by the linking together
of ethylene molecules (C_2H_4).
ICI Plastics Division...



The packing together of giant molecules is important in such substances as plastics. These are also giant molecules built up from small molecular units (see the Background Book *Plastics*). The long-chain molecules are all tangled together in a disorderly way, so that the structure of plastics tends to be rather amorphous than crystalline. To convert a plastic (for example, nylon) into a strong fibre for making clothes, threads of it are stretched to several times their original lengths to bring the long-chain molecules into orderly alignment, similar to the orderly packing of atoms and molecules in crystals. The 'crystalline' filaments formed by stretching are very much stronger.

Questions

1. What is our picture of the particles in a solid, a liquid, and a gas?
2. What factors other than how close the particles are packed affects the density of a substance?
3. What simple evidence is there for the fact that ice is less dense than water? What does it signify about the molecules in the water and does it apply to water at all temperatures?
4. Find out the packing structure of the particles in the following substances:
potassium chloride, chromium, zinc, caesium chloride, ice, diamond.
See if you can get hold of polystyrene spheres to make some of these structures
5. Give examples of some of the ways in which their structure influences the properties of substances.



Chemistry Background Books

General editor H P H Oliver Author of this Book C V Platts

Art editor Ivan Dodd

Published for the Nuffield Foundation by Longmans/Penguin Books

Longmans Green and Co Ltd 48 Grosvenor Street London W1

Penguin Books Ltd Harmondsworth Middlesex England

© Nuffield Foundation 1967 First published 1967

Made and printed in Great Britain by Newgate Press Limited

CBB04333

